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Potential use of real-time dissolved oxygen sensors for oxygen scavenging feedback control

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Abstract. The North Sea oil and gas sector has been operational since the 1970's and the natural pressure in the reservoirs has been gradually decreasing, which has led to an increased use of water injection to facilitate the required pressure for oil and gas extraction. This involves high pressure and flow of sea water, which is transported through the offshore facilities and due to the corrosive environment, it introduces corrosion. One of the main culprits is dissolved oxygen, which the offshore operators actively remove with vacuum and chemical oxygen scavengers. The vacuum deaerators have a removal limit, after which the dissolved oxygen concentration is decreased using chemical oxygen scavengers most often sodium sulfite, but this adds a cost. The main expense is not the chemical itself, but the side product of the chemical reaction, which leaves sulfates, that feed sulfate reducing bacteria, leading to a production of Hydrogen sulfide which leads to sour corrosion. One solution to reduction in dissolved oxygen and oxygen scavenger is proper control of the facilities. This work investigates the potential for feedback control of the facilities using an online dissolved oxygen instrument, where an experimental study of three commercial dissolved oxygen instruments has been performed, with good results.

1. Introduction

The Danish North Sea offshore oil and gas industry has been operational since the early 1970's, where most of the reservoirs are old and require secondary recovery, which in this case is water injection with fresh sea water. Due to the aging reservoirs, the increase in water injection has been continuous and in 2014 the injection volume was 3.5 times larger than the oil volume that was produced [1]. This increasing amount of water required for injection must be processed by the water injection facilities, a typical offshore water injection process with a deaeration facility, is sketched in the block diagram in figure 1.

The water is pumped close to the ocean's surface, where the dissolved oxygen (DO) levels are high. Under normal conditions, water saturated with air would have a concentration in the following range [5 mg/l - 8 mg/l] [2]. DO poses a corrosion threat to the facilities as pipes and equipment in most cases are made from steel and carbon steel [3]. Previous studies show that DO levels above [0.02 mg/l - 0.05 mg/l] greatly benefit oxygen accelerated corrosion [4], [5], [6]. Steel corrosion rate at 5-8 mg/l of DO is [0.25 mm/yr - 15 mm/yr], where for DO concentrations below 10 µg/l the corrosion rate is decreased to 0.01 mm/yr, [2]. According to [7], the estimated cost of corrosion in the United States is 170 billion USD per year, and a reduction in corrosion would contribute greatly to a leaner operation.

In order to keep the system corrosion free, it can be operated oxygen free, but if only vacuum towers are used the system cannot be operated below 0.3 mg/l DO [4]. To achieve even lower DO levels oxygen scavenger is injected [8], and depending on the amount, the DO level can be reduced to 0 mg/l. The side effect of reducing the DO with an oxygen scavenger is that the most oxygen scavengers are sulfite based [9], which is converted into H_2S by sulfate reducing bacteria [10], [3].

The production of H_2S occurs in several steps, first the oxygen scavenger, is reduced to SO_4^{2-} following the reaction shown in equation 1. Now, if the DO levels are significantly low, sulfate reducing bacteria will use SO_4^{2-} in the sulfur cycle and produce H_2S, following the reaction in equation 2.

$$SO_3^{2-} + O_2 \rightarrow SO_4^{2-} \quad (1)$$

$$SO_4^{2-} \rightarrow H_2S \quad (2)$$

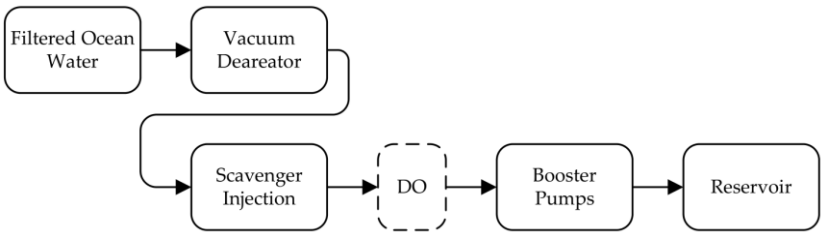

Figure 1. Block diagram of an offshore water injection facilities deaeration system. The placement of a potential DO instrument is indicated with a dotted lined block.

The production of H_2S is accelerated with the lowering of DO when the DO level is decreased below 40µg/l [7]. Figure 2 is a simplified sketch of the occurrence of sweet and sour corrosion depending on the oxygen level with a theoretical optimal range.

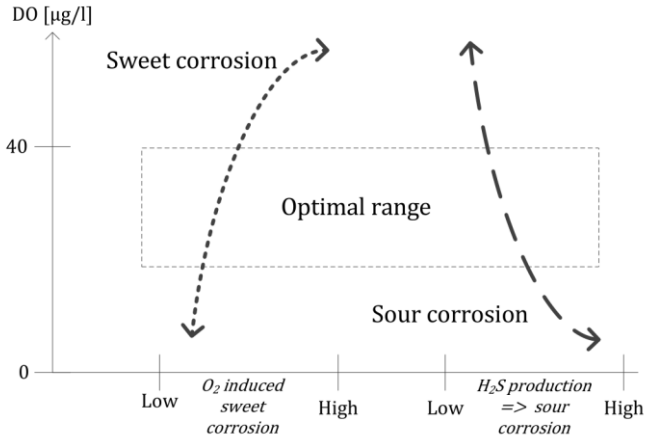

Figure 2. Simplified corrosion chart illustrating the areas of sweet and sour corrosion and the desirable operating range.

This range is hypothetical and since if the oxygen level is kept below a specific point the sweet corrosion is reduced, while keeping it from a too low level reduces sour corrosion. In order to keep the system within this narrow operating range, the system must be controlled, where one solution is to control the flow rate of the oxygen scavenger injection.

In order to do this the DO concentration should be measured and used as a feedback in a oxygen scavenger control loop, [11]. A potential control loop has been sketched in figure 3, where DO is measured downstream of the vacuum deaerator and the oxygen scavenger injection.

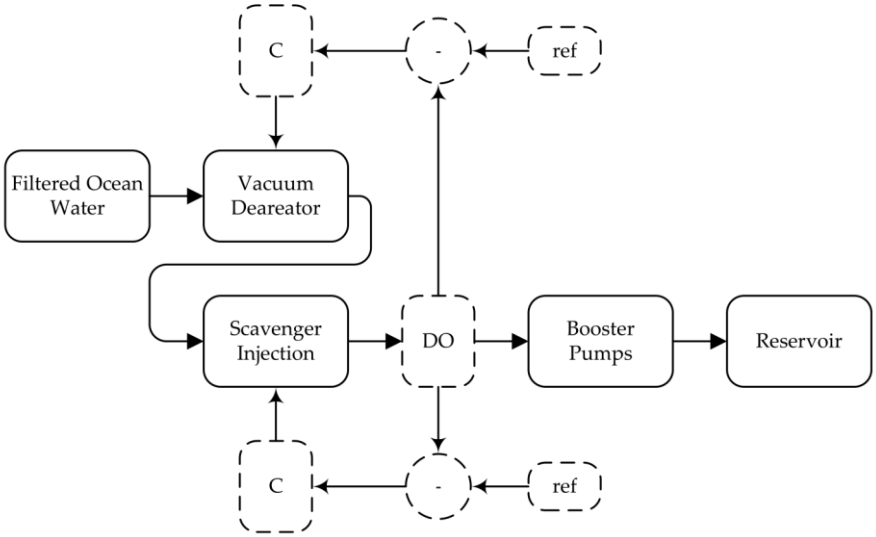

Figure 3. Block-diagram of a potential control solution for the deaeration facility, where DO is used as a feedback to control the vacuum de-aerator and the oxygen scavenger injection.

The constraints for this problem are:

- Maintain the DO below the desired reference
- Subjected to minimizing oxygen scavenger injection

The goal is thus to design a control loop for the deaeration facility, including the oxygen scavenger injection and the vacuum deaerator, where the aim is to use real-time DO measurements as the feedback. The benefit of real time feedback control of the DO is that it will reduce the over or under injection of the oxygen scavenger. The current systems are operated with the strategy to reduce the DO to a minimum, i.e. below 40 µg/l, such that the corrosion is reduced to a minimum. We believe that by controlling the DO at a specific set-point, scavenger injection can be more precisely controlled which will reduce the side effects of over or under injection of the oxygen scavenger.

Any potential control strategy depends on reliable measurement of DO, and current North Sea oil and gas water injection facilities do not take advantage of DO instruments for feedback purpose in deaeration control. Instead these systems are in most cases operated based on feed forward strategies where the operator uses manual samples of DO, to adjust oxygen scavenger injection while the vacuum deaerator is kept at a constant vacuum. The oxygen scavenger injection flow rate is set to be proportional to the water flow rate. This can in some cases introduce either too high DO concentration in the water, which results in corrosion and bacterial growth, or it can introduce a too high oxygen scavenger concentration in the water, introducing sour corrosion [12], [13].

This leads to the motivation for investigation of the ability of DO instruments to measure DO in real-time. In this work three DO instruments, from three different manufactures, using two different technologies, optical and electrochemical, are evaluated with respect to their applicability for use in deaeration applications in the offshore oil and gas industry.

An experimental analysis of three industrial DO instruments is performed, aiming to investigate the DO instrument's ability to measure DO levels close to 0 µg/l and dynamic changes in the DO concentration in seawater.

2. Experimental investigation

In order to investigate the DO instrument's ability to measure low DO concentrations and their transient performance, an experimental investigation was conducted. For this a pilot plant was

designed and constructed by an offshore contractor, Hytor A/S. This pilot plant was designed for offshore use, and a few modifications were made for its use onshore in our laboratory.

2.1. Pilot plant setup

The pilot plant is an ATEX certified setup, which contains a set of three DO instruments specified in table 1, consisting of: Barben 4401 Oxy-Trace v4 (Barben), Hach Orbisphere A1100 (Hach) and Honeywell DL5000 (Honeywell). As the instruments are flow dependent, a flow controller was installed on the inlet to ensure a consistent flow rate through the instruments. The pilot plant is designed to operate on a side-stream, although in the laboratory set-up it was applied in-line to the main flow. The flow was facilitated by a frequency controlled centrifugal pump (Grundfoss CRE), with a buffer tank of 25 liters, although during the experiments the water quantity was kept at 15 liters. Data was collected using an ALMEMO 8590-9 I/O unit, with a sampling rate of 0.2 Hz. The testing facility is sketched in figure 4.

Table 1. DO instruments and the specifications.

Manufacturer	Instrument Name	Technology	T_r [T90]	Accuracy	Range
Barben	4401 Oxy-Trace v4	Optical	<30s	1 µg/L	1 - 1800 µg/L
Hach	Orbisphere A1100	Electrochemical	7.2s	0.1 µg/L	0-20 µg/L
Honeywell	DL5000	Electrochemical	60s	2 µg/L	–

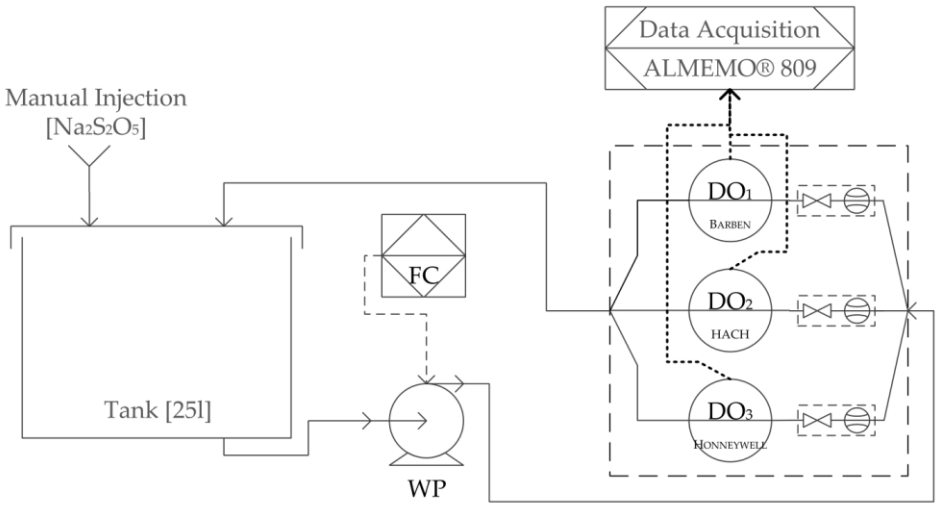

Figure 4. Simplified P&ID diagram of the DO testing facility.

The aim of the experiments was to analyze the steady state and dynamic response of the DO instrument under close to real-life conditions. To enable the most realistic scenario, the experiments were performed using ocean water which was collected from one of Danish North Sea water injection facilities. During the experiments the water temperature was measured to be $22.8°C$, the pH to 7.5 and the salinity to 3.35 mg/l.

Table 2. Chemicals.

Water properties	**Temperature**	**pH**	**Salinity**
	22.8 ◦C	7	50.97 mS/cm ≈ 33.5 PPT
Oxygen scavenger properties	**Name**	**CAS**	**Chemical formula**
	DiSodium Bisulfite	7681-57-4	$[Na_2S_2O_5]$

During the experiment the oxygen scavenger was added to the ocean water, see table 2 for characteristics, aiming to reach 0 µg/l DO concentrations. The data from the DO instruments was collected before, during and after the oxygen scavenger injection, to enable steady state and transient analysis. The injections of the oxygen scavenger are marked by the dashed line in figures 5, 6 and 7. After injection of the oxygen scavenger the water is continuously recirculated in the system by the pump at a consistent flow rate (specified by the supplier of the DO instruments to 200ml/min), which in addition ensured the mixing of the oxygen scavenger.

2.2. Oxygen scavenger injection

The oxygen scavenger was injected manually, aiming at keeping the DO concentration as low as possible. Due to the manual injection and monitoring, the DO concentration could not be kept between 0 and the desired range of 4 µg/l, and it drifts to around 1000 µg/l.

The oxygen scavenger quantity was manually measured on a scale, and then poured into the tank and stirred for 15 seconds. The amount of the oxygen scavenger added to the water was 1.5 g, for a total water volume of 15l. This is based on the theoretical dosage multiplied by a scaling factor, where the theoretical dosage was calculated using equations 3 and 4, refer to [14] and [15]. Where the chemical reaction of the oxygen scavenger with the oxygen is:

$$2\,Na_2SO_3 + O_2 \rightarrow 2Na_2SO4 \tag{3}$$

and the theoretical dosage can be calculated to:

$$2(126\ \text{g/mole}\ Na_2SO_3) = 7.88 \cdot \text{theoretical}\ 32\ \text{g/mole}\ O_2 \tag{4}$$

In the experiments this theoretical concentration was not enough to reduce the DO concentration to near 0 mg/l, and the concentration of oxygen scavenger was multiplied by a scaling factor of 2.5 to achieve the desired DO concentration.

3. Results

The results show a consistent steady state measurement from all three instruments when the DO concentrations are close to 0 µg/l, with a relatively low offset in the Barben's and Honeywell's output, 2 µg/l and 0.5 µg/l respectively. Where the Barben performs best, is that it continuously measures a low change in the concentration, closely followed by the Honeywell. The Hach is believed to have saturated as it measures a consistent 0 µg/l, which caused by the instrument's discretization of the analogous signal where the step was approximated to 12.5 µg/l.

At higher DO concentrations the offset is more prominent, where the three instruments start showing significant differences, e.g. after 45 hours in figure 5. What is observed is that the offset increases with the DO concentrations, which would indicate a non-linear behavior when the instruments move away from their nominal operating point which is around 0-40 µg/l, the point where the instruments were calibrated.

The dynamic response of the instruments, when considering the DO saturation, is consistent for the three measurements when the DO is decreasing and is inconsistent when the DO is increasing. The Barben and Hach show similar transient behavior during the increase in DO, whereas the Honeywell has a delay of 5 hours after which it follows the measurements of the Barben and the Hach. This is most likely caused by lower resolution, where the Honeywell has difficulty tracking concentrations below ≈ 10-15 µg/l, which acts as a hysteresis.

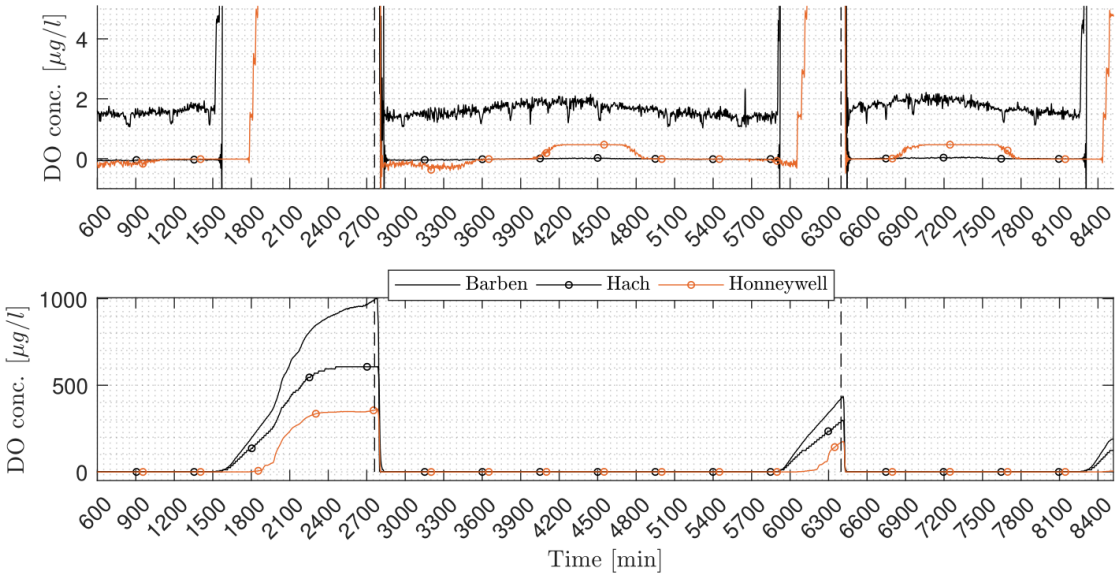

Figure 5. DO concentration, data collected over a period of 142 hours, from the three instruments. The top plot shows DO concentration in the range from 0-5 µg/l and the bottom plot shows the measured range, 0-1000 µg/l.

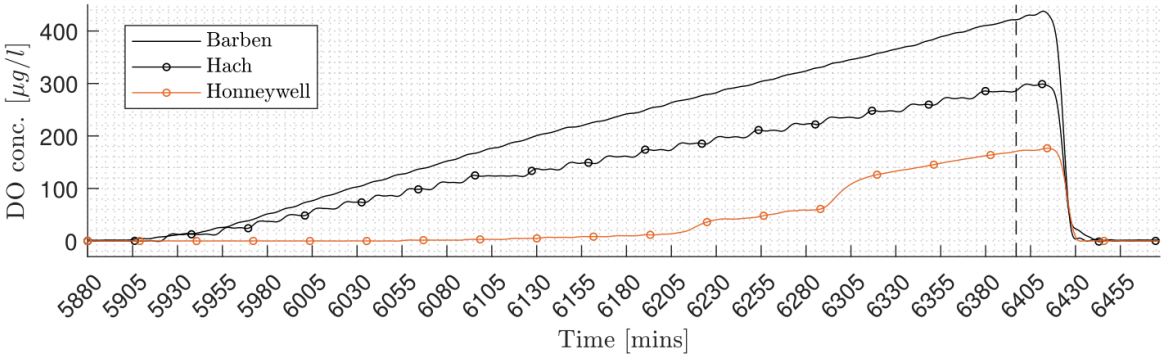

Figure 6. Dynamic Behavior of the DO concentration, showing saturation of DO and the second oxygen scavenger injection (1.5g), a zoom-in at time [5880-6460] min.

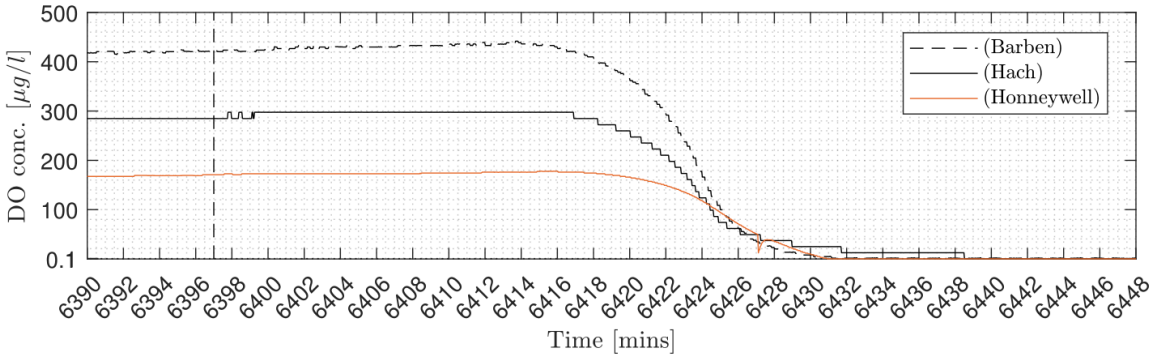

Figure 7. Dynamic Behavior of the DO concentration, second oxygen scavenger injection (1.5g), a zoom-in from 6409 min.

During the DO decrease the delay is not observed, which is due to the faster transient behavior with respect to oxygen scavenger injection (indicated with the dashed vertical lines), shown in figure 7, which, due to the reaction time of the oxygen scavenger, occurs much faster than the saturation of the water with the oxygen. It is noteworthy that the transients and the delay in the data are a sum of the chemical reaction time and the instrument's reaction time. Where the chemical reaction time is affected by multiple parameters such as: salinity, temperature, stirring intensity and the concentration of the oxygen scavenger [16]. In the case of figure 7, the reaction time from injection to minimum DO level is 34 min, if data from the Barben is used.

4. Discussion of results and the potential for feedback control

If the DO instruments are to be used for feedback control, with the goal of controlling a DO reference of about [10-40] µg/l, the instruments must satisfy two main requirements. First is to be able to detect the desired DO range, [10-40] µg/l, second the bandwidth of the instrument must be faster than the system's bandwidth.

Hach measurements have a resolution of roughly 12.5 µg/l, which results in saturation of the measurements around 0 µg/l, and poor performance at concentrations below 40 µg/l, refer to figure 7. This is not the case with the other two instruments, although the Honeywell, suffers from delay, especially during increasing DO levels. The measurements done with the Barben can satisfy the first of these two requirements, where the DO is continuously measured at very low concentrations, below 4 µg/l.

The second requirement cannot be directly quantified in the laboratory, as the bandwidth of the pilot plant is inconsistent with the real-life platform, and the bandwidth would have to be quantified in the field. The main difference between the pilot plant and the real offshore installation is that the pilot plant operates as a batch process, where the water is recirculated, giving the oxygen scavenger time to react on the same water to which it was added, and thus the residence time is equal to the duration time of the experiment.

In the offshore system the injection water is continuously pumped and processed with a constant oxygen scavenger injection. The residence time in this scenario will be determined by the flow rate, and the volume of the pipe and the measured DO will be determined by the precise placement of the instruments. If the flow rate and the volume of the pipelines are known, then the experiments can be replicated in the laboratory, by scaling the pipeline size and flow, whilst achieving the required residence time. By applying a continuous sampling, using a controllable injection pump, the correct amount of oxygen scavenger can be injected, and the bandwidth of the open-loop system can be determined, which we will refer to as the oxygen scavenger injection system. If the bandwidth of the DO instruments is two times faster than the bandwidth of the oxygen scavenger injection system, the DO instruments could potentially be used for feedback control of the oxygen scavenger injection. This of course requires that the open loop system is monitored using a fast responding DO instrument, which has a guaranteed faster bandwidth than the considered system.

From earlier experiments we have observed a bandwidth of oxygen absorption in a waste water treatment plant, where a commercial DO instrument, Hach (Orbisphere-M1100), was used to record the DO concentration, the result is shown in figure 8. The measured DO concentration changes from 0 to 800 µg/l in ≈ 2 min, upon opening of the valve (at time [09:59:37]) which sends in oxygen to saturate an activated sludge mixture. The initial delay is caused by a delay in the air supply system, which accounts for a few minutes, after which the DO instrument tracks the change in the DO concentration. These results show that commercial DO instruments are capable of measuring faster transient than what was observed in this work. The main reason for the faster response is the faster dynamic of the activated sludge process.

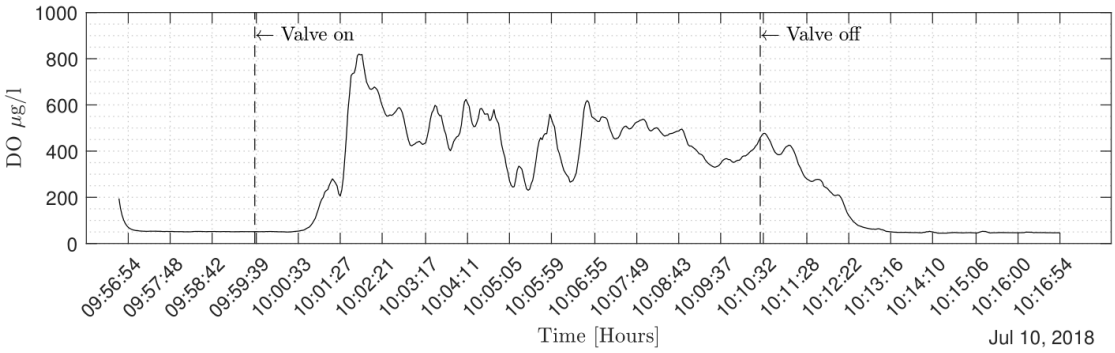

Figure 8. DO oxygen measurement at one Danish waste water treatment facility.

5. Conclusions

This paper successfully measured dissolved oxygen concentrations in seawater, collected from a Danish offshore water injection facility, at concentrations below 40 µg/l. In addition, it was possible to measure the transient of the oxygen scavenging, when applying an oxygen scavenger to the oxygen saturated sea-water. This investigation shows that the instruments that were used have potential for measuring low dissolved oxygen concentrations and their transients. Further investigations are required to quantify the dynamics of the offshore oxygen scavenging system, in order to determine if the current DO instruments can track the system's dynamic and thus can potentially be used for feedback purposes.

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